



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

REC'D 20 OCT 2004

WIPO

PCT

Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03253365.5

**PRIORITY
DOCUMENT**

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Anmeldung Nr:
Application no.: 03253365.5
Demande no:

Anmeldetag:
Date of filing: 29.05.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ B.V.
Carel van Bylandtlaan 30
2596 HR Den Haag
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

A process for the removal of SO₂, HCN and H₂S and optionally COS, CS₂ and NH₃
from a gas stream

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

B01D53/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI



TS 1086 EPC

Iye

A PROCESS FOR THE REMOVAL OF SO₂, HCN AND H₂S AND
OPTIONALLY COS, CS₂ AND NH₃ FROM A GAS STREAM

FIELD OF THE INVENTION

The invention relates to a process for removing SO₂,
HCN and H₂S and optionally COS, CS₂ and NH₃ from a gas
stream.

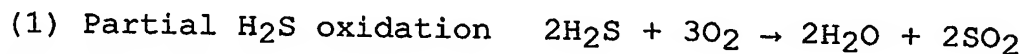
5 BACKGROUND OF THE INVENTION

The removal of sulphur compounds such as SO₂ and H₂S
from a gas stream comprising these compounds is of
considerable importance, because the toxicity and smell
of sulphur compounds renders their presence highly
10 undesirable.

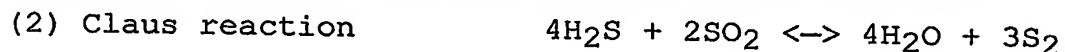
Gas streams from industrial chemical processes may
contain a variety of sulphur compounds such as H₂S, SO₂,
CS₂ and COS. In addition, other compounds whose presence
is undesirable may be present such as HCN or NH₃. It is
15 often necessary for the intended purposes of the gas
stream to remove these compounds at least partly, for
example to prevent catalyst poisoning in processes after
the gasification stage.

Processes for the removal of sulphur compounds are
20 known in the art. In EP 324,526 a process is described
for the removal of H₂S, COS, CS₂ and SO₂ from a gas
stream, by converting COS and CS₂ into H₂S. Although
EP 324,526 mentions that the removal of H₂S can be
achieved, it does not specify the preferred type of
25 process for H₂S removal, nor is the concentration of H₂S
in the treated gas stream mentioned.

A process known in the art for the removal of H₂S from a gas stream is the partial oxidation of H₂S to SO₂ according to:



5 The SO₂ formed can be (catalytically) converted to elemental sulphur according to the Claus reaction:



10 This process is known as the Claus process. The Claus process is frequently employed both in refineries and for the processing of H₂S recovered from natural gas. A disadvantage of the Claus process is that it is thermodynamically limited by the increase of the water vapour content and simultaneously by the decrease of the H₂S and SO₂ concentration as the H₂S conversion proceeds, with the result that the equilibrium of the Claus
15 reaction shifts to the left. Since the dew point of water lies below the solidification point of sulphur, condensation of the water vapour in the process gas to remove this limitation can lead to serious problems, such
20 as clogging due to the solidification of sulphur and corrosion due to the formation of sulfuric acid, causing serious operational problems.

25 Another disadvantage of the Claus process is that the concentration of H₂S in the treated gas is still relatively high. The Claus process has been improved to an extent where the H₂S content of the treated gas can be lowered to approximately 1 vol% (Superclaus-99 process) and the SO₂ content to approximately 0.02 vol%. However, especially in the case where it is necessary to comply
30 with requirements with regard to residential use or environmental regulations with respect to emission of sulphur compounds, even lower concentrations of H₂S and

SO₂, in the ppm range, have to be achieved. A disadvantage of the Claus and Superclaus process is that such low concentrations of H₂S and SO₂ cannot be achieved.

5 The removal of HCN from gas streams is important not only because of its own toxic properties, but also in view of corrosive NO_x compounds which can evolve when both HCN and oxygen are present in a gas stream. In addition, HCN itself is corrosive to equipment when
10 allowed to concentrate in liquid streams upon gas treating.

 We have now found a relatively simple and inexpensive process for removing SO₂, H₂S and HCN and optionally COS, CS₂ and NH₃ from a gas stream. In the process according
15 to the invention, a combination of reaction steps is used to achieve the removal of sulphur compounds such as H₂S and SO₂, and optionally also COS and/or CS₂, as well as HCN from a gas stream comprising these compounds, to concentrations of below 10 ppmv for H₂S, below 100 ppmv
20 for SO₂ and below 0.01 vol%, preferably 10 ppmv for HCN.

 Another advantage of the process according to the invention compared to the Claus process is that it is not necessary to produce a gas with a high H₂S content, for example by amine treatment, prior to H₂S removal. In the
25 Claus process, a pretreatment to produce a gas with a high H₂S content is necessary to make the gas suitable as a Claus feed.

 Yet another advantage of the process according to the invention is that the problem of sulphur clogging -as
30 observed in other liquid based sulphur recovery processes- is substantially less or absent due to the hydrophilic nature of the sulphur formed.

SUMMARY OF THE INVENTION

The invention relates to a process for the removal of SO_2 , HCN and H_2S and optionally one or more compounds from the group of COS , CS_2 and NH_3 from a first gas stream, which process comprises the steps of:

(a) removing SO_2 from the first gas stream by contacting the first gas stream in a hydrogenation zone with a hydrogenation catalyst to obtain a second gas stream;

(b) removing HCN and optionally COS and/or CS_2 from the second gas stream obtained in step (a) by contacting the second gas stream in a hydrolysis zone with a hydrolysis catalyst to obtain a third gas stream;

(c) removing NH_3 from the third gas stream by contacting the third gas stream in a NH_3 -removal zone with an aqueous (acidic) washing liquid to obtain an ammonium-comprising aqueous stream and a fourth gas stream;

(d) removing H_2S from the fourth gas stream by contacting the fourth gas stream in a H_2S -removal zone with an aqueous alkaline washing liquid to obtain a H_2S -depleted gas stream and a hydrogen-sulphide-comprising aqueous stream;

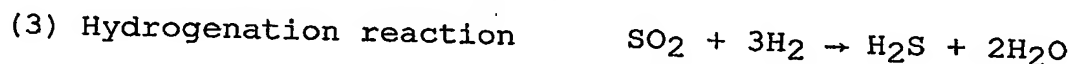
(e) contacting the hydrogen-sulphide-comprising aqueous stream obtained in step (d) with sulphide-oxidizing bacteria in the presence of oxygen in an oxidation reactor to obtain a sulphur slurry and a regenerated aqueous alkaline washing liquid;

(f) separating at least part of the sulphur slurry obtained in step (e) from the regenerated aqueous alkaline washing liquid and;

(g) recycling regenerated aqueous alkaline washing liquid obtained in step (e) to the H₂S-removal zone in step (d).

DETAILED DESCRIPTION OF THE INVENTION

5 In step (a) of the process according to the invention, SO₂ is removed from the first gas stream by contacting the first gas stream in a hydrogenation zone with a hydrogenation catalyst to obtain a second gas stream. In the hydrogenation zone, SO₂ is converted to
10 H₂S according to reaction (3):



Reference herein to a first gas stream is to a gas stream comprising H₂S, SO₂, HCN and optionally COS, CS₂ and NH₃ or combinations thereof. The total concentration
15 of sulphur compounds in the first gas stream is suitably between 10 ppmv and 30 vol%, preferably between 100 ppmv and 20 vol%, based on the total gas stream. The total concentration of HCN in the first gas stream is typically
20 between 10 and 5000 ppmv, suitably between 20 and 1000 ppmv, or between 40 and 250 ppmv, based on the total gas stream.

Suitably, the load of sulphur compounds in the hydrogenation zone is between 50 and 50000 kg/day.

25 Optionally, solid compounds present in the first gas stream can be removed from the first gas stream prior to entering the hydrogenation zone, for example by use of a filter.

The hydrogenation zone can be a gas/solid contactor, preferably a fixed bed reactor. Suitable hydrogenation
30 catalysts are for example cobalt/molybdenum or nickel/molybdenum catalysts. The hydrogenation catalysts suitable for the process according to the invention can

be supported, preferably on a refractory oxide support, more preferably on an alumina support.

5 Suitably, the temperature in the hydrogenation zone is between 200 °C and 380 °C, preferably between 210 °C and 330 °C, more preferably between 250 °C and 350 °C. The pressure in the hydrogenation zone is suitably between 1 and 100 bara, preferably between 2 and 80 bara.

10 Reference herein to a second gas stream is to a gas stream wherein the concentration of SO₂ is below 100 ppmv, preferably between 0.001 ppmv and 100 ppmv, more preferably between 0.01 ppmv and 50 ppmv, suitably between 0.1 ppmv and 15 ppmv, especially between 0.5 ppmv and 10 ppmv, based on the total gas stream.

15 In step (b) of the process according to the invention, HCN and optionally COS and/or CS₂ are removed from the second gas stream obtained in step (a) by contacting the second gas stream in a hydrolysis zone with a hydrolysis catalyst to obtain a third gas stream.

20 In the hydrolysis zone, HCN and, if applicable, COS and/or CS₂ are converted according to the following reactions:



30 The amount of water/steam in the hydrolysis zone is preferably between 10 v/v% and 80 v/v%. Optionally, water or steam of a mixture thereof may be added to the second gas stream prior to contacting the second gas stream with the hydrogenation catalyst. Preferably, the amount of water/steam added is such that the water/steam content of the first gas stream is between 10 v/v% and 80 v/v%, preferably between 20 v/v% and 70 v/v%, more preferably

between 30 v/v% and 50 v/v%, based on steam. Typically, the reaction conditions are selected in such a way, that the reaction mixture remains below the dewpoint of H₂O.

5 If COS and/or CS₂ are present, the total concentration of COS and CS₂ in the second gas stream is suitably between 10 ppmv and 2 vol%, preferably between 20 ppmv and 1 vol%, based on the total gas stream.

10 The hydrolysis zone can be a gas/solid contactor, preferably a fixed bed reactor. Catalysts for the hydrolysis of HCN and optionally COS and/or CS₂ are known to those skilled in the art and include for example TiO₂-based catalysts or catalysts based on alumina and/or chromium-oxide. Preferred catalysts are TiO₂-based catalysts.

15 Optionally, the hydrolysis step can be done prior to the hydrogenation step. A disadvantage of performing the hydrogenation step prior to the hydrolysis step is that when a TiO₂ catalyst is used, the TiO₂ catalyst can also catalyze the Claus reaction, leading to the formation of sulphur from H₂S and SO₂. However, in the case where the temperature is above the dew point of sulphur, the formation of sulphur from the Claus reaction does not lead to clogging.

20 Reference herein to a third gas stream is to a gas stream wherein the concentration of HCN is below 0.01 vol%, suitably between 0.1 ppmv and 0.01 vol%, preferably between 1 ppmv and 50 ppmv, based on the total gas stream.

30 The concentration of COS, if present, in the third gas stream is below 0.01 vol%, suitably between 10 ppmv and 0.01 vol%, preferably between 15 ppmv and 100 ppmv, based on the total gas stream.

The concentration of CS_2 , if present, in the third gas stream is below 0.01 vol%, suitably between 1 ppmv and 0.01 vol%, preferably between 2 ppmv and 50 ppmv.

5 An advantage of the process according to the invention is that the third gas stream obtained after the catalytic hydrogenation (step a) and the hydrolysis (step b) can be treated directly with an aqueous alkaline washing liquid followed by contacting the alkaline hydrogensulphide containing washing liquid with sulphide-oxidizing bacteria in the presence of oxygen to obtain a sulphur slurry. For other processes such as the Claus process it is necessary that first by amine treatment and regeneration a sour gas is produced that has a high H_2S content to make it suitable as a Claus feed.

10 In step (c) of the process according to the invention NH_3 is removed from the third gas stream by contacting the third gas stream in an NH_3 -removal zone with an aqueous (acidic) washing liquid to obtain an ammonium-comprising aqueous stream and a fourth gas stream. The amount of NH_3 is suitably between 10 and 6000 ppmv, preferably between 20 and 2000 ppmv. The temperature in the NH_3 -removal zone is suitably between 5 and 70 °C, preferably between 10 and 50 °C. The pressure in the NH_3 -removal zone is suitably between 1 and 100 bara, preferably between 2 and 80 bara.

25 In step (d) of the process according to the invention H_2S is removed from the fourth gas stream by contacting the fourth gas stream in H_2S -removal zone with an aqueous alkaline washing liquid to obtain a H_2S -depleted gas stream and a hydrogen-sulphide-comprising aqueous stream.

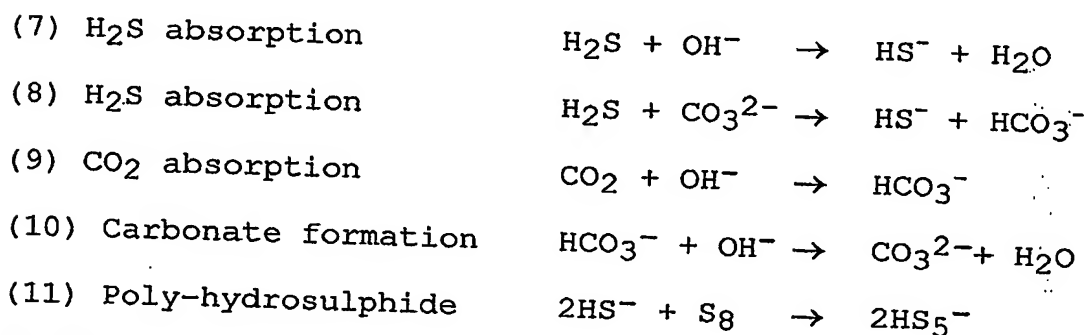
30 Suitably, the load of sulphur compounds in the H_2S -removal zone is below 60000 kg/day, or between 50 and

50000 kg/day, preferably between 75 and 20000 kg/day, more preferably between 100 and 10000 kg/day.

Suitably, the total amount of H₂S of the fourth gas stream is between 10 ppmv and 20 vol%, preferably between 20 ppmv and 10 vol%.

Suitable aqueous washing liquids include aqueous hydroxide solutions, e.g. sodium hydroxide or potassium hydroxide solutions in water. The pH of the aqueous alkaline solvents is suitably between 7 and 12, preferably between 8 and 11.

The main reactions that can take place in the H₂S-removal zone in step (d) are:



The term sulphide-comprising aqueous stream as used herein refers to an aqueous stream comprising one or more products of the main reactions (7) to (11) that can take place in the H₂S-removal zone, such as HS⁻, disulphides, polysulphides, thiocarbonates and carbonates but can also include dissolved H₂S.

Due to their odorous nature, H₂S, mercaptans, sulphides, disulphides and aromatic mercaptans can be detected at parts per million concentrations. Thus, it is desirable for users of such gas and refinery streams to have total concentration of sulphur compounds, especially H₂S, lowered to a concentration of e.g. less than 30 or

20 ppmv, preferably less than 10 ppmv, based on the total H₂S-depleted gas stream.

5 Reference herein to "H₂S-depleted gas stream" is to a gas stream wherein the total concentration of sulphur compounds, especially H₂S, is below 30 ppmv, suitably between 0.01 and 30 ppmv, or below 20 ppmv, suitably between 0.01 and 20 ppmv, or below 10 ppmv, suitably between 0.01 and 10 ppmv, preferably between 0.05 and 3.5 ppmv, more preferably between 0.1 and 1 ppmv, based
10 on the total gas stream.

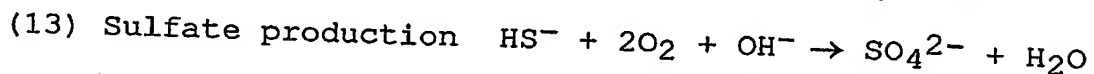
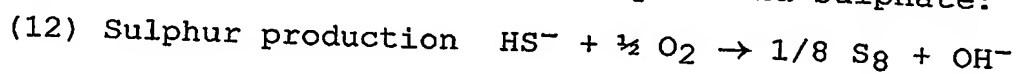
The preferred temperature in the H₂S removal zone is between 5 and 70 °C, more preferably between 10 and 50 °C. Preferably, the pressure in the H₂S removal zone is between 1 and 100 bara, more preferably between 2 and
15 80 bara.

Typically, the H₂S removal zone is a gas/liquid contactor. Suitable gas/liquid contactors are described in Perry's Chemical Engineers' Handbook, 7th edition, section 14 (1997) and include for example a tray or
20 packed column or a gas scrubber.

Optionally, the medium of the H₂S removal zone is buffered. Preferred buffering compounds are carbonates, bicarbonates phosphates and mixtures thereof, especially sodium carbonate and/or sodium bicarbonate. The
25 concentration of the buffering compounds depends inter alia on the composition of the gas flow and is generally adjusted in such a way, that the pH of the reaction medium in the H₂S removal zone is between 5.5 and 10, more preferably between 6.5 and 9.

30 In step (e) of the process according to the invention the hydrogen-sulphide-comprising aqueous stream obtained in step (d) is contacted with sulphide-oxidizing bacteria

in the presence of oxygen in a oxidation reactor to obtain a sulphur slurry and a regenerated aqueous alkaline washing liquid. The main reaction that can take place in the oxidation reactor in step (e) is the microbiological formation of sulphur and sulphate:



The term sulphur slurry as used herein refers to a slurry comprising one or more products of the main reactions, including reactions (12) and (13), that can take place in the oxidation reactor.

The term regenerated aqueous alkaline solvent as used herein refers to an aqueous alkaline solvent wherein at most 2 w/w% impurities are present, preferably at most 1 w/w%.

Reference herein to sulphide-oxidizing bacteria is to bacteria which can oxidize sulphide to elemental sulphur. Suitable sulphide-oxidizing bacteria can be selected for instance from the known auto tropic aerobic cultures of the genera Thiobacillus and Thiomicrospira.

Typical pressures in the oxidation reactor in step (e) are between 1 and 2 bara.

Suitably, the oxidation reactor has a volume of between 5 and 2500 m³, preferably between 10 and 2000 m³.

Preferably, the reaction medium in the oxidation reactor in step (e) is buffered. The buffering compounds are chosen in such a way that the bacteria present in the oxidation reactor tolerate them. Preferred buffering compounds are carbonates, bicarbonates phosphates and mixtures thereof, especially sodium carbonate and/or sodium bicarbonate. The concentration of the buffering compounds depends inter alia on the composition of the gas flow and is generally adjusted in such a way, that

the pH of the reaction medium in the oxidation reactor is between 5 and 10, more preferably between 6 and 8.

5 In step (f) of the process according to the invention at least part of the aqueous sulphur slurry obtained in step (e) is separated from the regenerated aqueous alkaline solvent. The phrase "at least part of" as used herein is to indicate that between 1 and 100%, preferably between 5 and 95 w/w%, more preferably between 10 and 90 w/w% of the sulphur is separated, based on the total weight of the slurry.

10 Suitably, the separating step takes place in a solid/liquid separator. Suitable solid/liquid separators are described in Perry's Chemical Engineers' Handbook, 7th edition, section 22 (1997).

15 Typically, the sulphur content of the separated aqueous sulphur slurry is between 5 w/w% and 50 w/w%, based on the slurry. Typically, the water of the sulphur slurry is removed to an extent that a sulphur cake with a dry solids content of between 55 and 70% is obtained. Typically, the sulphur purity of the sulphur cake is 20 between 90 and 98 w/w%, based on the total weight of the sulphur cake. Optionally, the sulphur slurry obtained in step (c) can be re-slurried, filtered and dried to obtain a sulphur paste with a purity of at least 95 wt% sulphur, preferably at least 99 wt% sulphur. The sulphur paste 25 thus-obtained can optionally be dried to produce a powder with a dry weight content of at least 85%, preferably at least 90%. This powder can suitably be applied as a fungicide or as a miticide.

30 The sulphur produced in the process according to the invention has a hydrophilic nature and does not cause the fouling problems that are typically caused by sulphur produced by non-biological liquid processes. Another

advantage of the sulphur produced in the process according to the invention is that it is very suitable for use as a fertilizer.

5 In step (g) of the process according to the invention, regenerated aqueous alkaline washing liquid obtained in step (e) is recycled to the H₂S-removal zone in step (d). Suitably, between 10 and 99%, preferably between 30 and 95%, more preferably between 40 and 90% of the total amount of regenerated aqueous alkaline washing
10 liquid obtained in step (e) is recycled to the H₂S-removal zone in step (d). By recycling the regenerated aqueous washing liquid to the H₂S-removal zone fresh aqueous washing liquid is supplied to the H₂S-removal zone for the removal of H₂S. This enhances the removal of
15 H₂S to a concentration of 30 ppmv or less, suitably 20 ppmv or less, preferably 10 ppmv or less.

The process according to the invention is especially suitable for the treatment of a gaseous CO-containing stream, especially a syngas stream, an offgas stream from
20 a carbon black plant, or a refinery gas stream. Syngas is a general term that is applied to mixtures of inert components, carbon monoxide, carbon dioxide and hydrogen that are derived from the gasification of coal, oil residues, waste or biomass. The main components of syngas
25 are hydrogen and carbon monoxide. Further, often carbon dioxide and traces of methane are present. Refinery streams concern crude oil derived gaseous streams containing smaller or larger amounts of sulphur compounds. Recycle streams and bleed streams of
30 hydrotreatment processes, especially hydrodesulfurisation processes, can also suitably be treated by the process according to the invention.

The invention will now be illustrated by means of schematic figure 1. Figure 1 depicts a typical process scheme according to the invention, wherein a gas stream comprising SO_2 , HCN , H_2S and optionally COS , CS_2 and NH_3 enters the hydrogenation zone (2) via line (1) and is contacted with the hydrogenation catalyst to remove the SO_2 . After treatment in the hydrogenation zone the second gas stream, which is SO_2 -depleted, leaves the hydrogenation zone via line (3) and enters the hydrolysis zone (4) where it is contacted with a hydrolysis catalyst to remove HCN and optionally COS and/or CS_2 . Optionally, steam or a steam/water mixture can be added to the hydrolysis zone via line (25). After treatment in the hydrolysis zone, the third gas stream, which is depleted of HCN , COS and/or CS_2 , leaves the hydrolysis zone via line (5) and enters the HN_3 -removal zone (6), where it is treated with aqueous (acidic) washing liquid to obtain an ammonium-comprising aqueous stream and a fourth gas stream. After treatment in the NH_3 -removal zone, the fourth gas stream, which is depleted of HCN , COS and/or CS_2 and NH_3 , leaves the HN_3 -removal zone via line (7) and enters the H_2S -removal zone (8), where it is contacted with an aqueous washing liquid. The H_2S -depleted gas stream is led from the H_2S -removal zone via line (9), optionally via a knockout vessel (10) and can be further processed via line (11). A sulphide-comprising aqueous stream leaves the H_2S -removal zone via line (12) and enters a flash vessel (13). H_2S -depleted excess gas is vented off from the flash vessel through line (14). In the case that flash gas contains some H_2S , the H_2S needs to be removed in a small flash gas contactor before

further use as fuel gas. The sulphide-comprising aqueous stream is led via line (15) to the aerobic reactor (16) where the sulphide compounds are oxidized. Nutrients and air are fed to the aerobic reactor via feed lines (17) and (18). The containing-containing solid/liquid mixture generated in the aerobic reactor is led via line (19) to a solid/liquid separator (20) where the solid containing is separated and discharged via line (21). The liquid is led back to the bioreactor via line (22). Off-gas is vented from the aerobic reactor via line (23). The regenerated aqueous alkaline solvent is led to the H₂S-removal zone via line (24).

The invention will now be illustrated by the following non-limiting examples.

EXAMPLE 1 (comparative)

A gas stream containing containing compounds and HCN with concentrations as given in table 1 is heated to a temperature of 280 °C and led to a reactor filled with a stacked bed of hydrogenation catalyst and hydrolysis catalyst. The gas is cooled in a quench tower at 40 °C and treated in an amine/Claus unit to remove the H₂S. The concentrations of containing compounds and of HCN in the treated gas is given in table 1.

Table 1

	Gas to treating system (v/v%)	Gas after treating system (v/v%)
H ₂ O	6.7	3.2
H ₂ S	1.9	0.01
SO ₂	0.1	0.05
CS ₂	0.09	0.01
COS	0.28	0.01
HCN	0.03	0.01
NH ₃	0.04	0.03

EXAMPLE 2 (according to the invention)

5 A gas stream containing containing compounds and HCN with concentrations as given in table 2 is heated to a temperature of 280 °C and led to a reactor filled with a stacked bed of hydrogenation catalyst and hydrolysis catalyst. The gas is cooled in a quench tower at 40 °C, treated in an NH₃-scrubber and subsequently treated in a H₂S-removal unit, followed by oxidation of the resulting hydrogensulphides in a bioreactor according to the
10 invention. The concentrations of the containing compounds and of the HCN in the treated gas is given in table 2.

Table 2

	Gas to treating system (v/v%)	Gas after treating system (v/v%)
H ₂ O	40	6.8
H ₂ S	0.9	0.0002
SO ₂	0.1	0.001
CS ₂	0.04	0.0002
COS	0.01	0.001
HCN	0.1	0.001
NH ₃	0.03	0.001

From the examples it is clear that with the process according to the invention a substantially lower concentration of containing compounds, especially of H₂S, SO₂, CS₂ and COS is achieved, while the concentration of HCN is also lowered.



C L A I M S

1. A process for the removal of SO_2 , HCN and H_2S and optionally one or more compounds from the group of COS , CS_2 and NH_3 from a first gas stream, which process comprises the steps of:
- 5 (a) removing SO_2 from the first gas stream by contacting the first gas stream in a hydrogenation zone with a hydrogenation catalyst to obtain a second gas stream;
- (b) removing HCN and optionally COS and/or CS_2 from the second gas stream obtained in step (a) by contacting the
- 10 second gas stream in a hydrolysis zone with a hydrolysis catalyst to obtain a third gas stream;
- (c) removing NH_3 from the third gas stream by contacting the third gas stream in a NH_3 -removal zone with an aqueous acidic washing liquid to obtain an ammonium-
- 15 comprising aqueous stream and a fourth gas stream;
- (d) removing H_2S from the fourth gas stream by contacting the fourth gas stream in a H_2S -removal zone with an aqueous alkaline washing liquid to obtain a H_2S -depleted
- 20 gas stream and a hydrogensulphide-comprising aqueous stream;
- (e) contacting the hydrogensulphide-comprising aqueous stream obtained in step (d) with sulphide-oxidizing bacteria in the presence of oxygen in an oxidation reactor to obtain a containing slurry and a regenerated
- 25 aqueous alkaline washing liquid;
- (f) separating at least part of the containing slurry obtained in step (e) from the regenerated aqueous alkaline washing liquid and;

(g) recycling regenerated aqueous alkaline washing liquid obtained in step (e) to the H₂S-removal zone in step (d).

2. A process according to claim 1, wherein the containing load in the H₂S-removal zone in step (d) is
5 between 50 and 50000 kg/day, preferably between 75 and 20000 kg/day, more preferably between 100 and 10000 kg/day.

3. A process according to claim 1 or 2, wherein the total concentration of containing compounds in the
10 treated gas, especially H₂S, is below 30 ppmv, preferably between 0.01 and 20 ppmv.

4. A process according to any of claims 1 to 3, wherein the washing liquid in step (d) is buffered, preferably at a pH of between 5.5 and 10, more preferably at a pH
15 between 6.5 and 9.

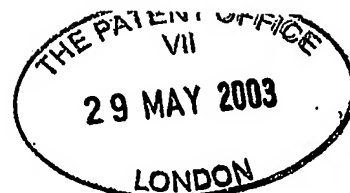
5. A process according to any of claims 1 to 4, wherein the contents of the oxidation reactor in step (e) is buffered, preferably at a pH between 5 and 10, more preferably between 6 and 8.

20 6. A process according to any of claims 1 to 5, wherein the oxidation reactor in step (e) has a volume of between 5 and 2500 m³.

7. A process according to any of claims 1 to 6, wherein the containing slurry obtained in step (e) is re-
25 slurried, filtered and dried to obtain a purity of at least 95 wt% containing, preferably at least 99 wt% containing.

8. A process according to any of claims 1 to 7, wherein water or steam or a mixture thereof is added to the
30 second gas stream prior to contacting the first gas stream in a hydrolysis zone with a hydrolysis catalyst in step (b).

- 5 9. A process according to claim 8, wherein the amount of water/steam added is such that the water/steam content of the second gas stream is between 10 v/v% and 80 v/v%, preferably between 20 v/v% and 70 v/v%, more preferably between 30 v/v% and 50 v/v%, based on steam%.



TS 1086 EPC

A B S T R A C T

A PROCESS FOR THE REMOVAL OF SO₂, HCN AND H₂S AND
OPTIONALLY COS, CS₂ AND NH₃ FROM A GAS STREAM

The invention relates to a process for the removal of SO₂, HCN and H₂S and optionally one or more compounds from the group of COS, CS₂ and NH₃ from a first gas stream, which process comprises the steps of:

- (a) removing SO₂ from the first gas stream by contacting the first gas stream in a hydrogenation zone with a hydrogenation catalyst to obtain a second gas stream;
- (b) removing HCN and optionally COS and/or CS₂ from the second gas stream obtained in step (a) by contacting the second gas stream in a hydrolysis zone with a hydrolysis catalyst to obtain a third gas stream;
- (c) removing NH₃ from the third gas stream by contacting the third gas stream in a NH₃-removal zone with an aqueous acidic washing liquid to obtain an ammonium-comprising aqueous stream and a fourth gas stream;
- (d) removing H₂S from the fourth gas stream by contacting the fourth gas stream in a H₂S-removal zone with an aqueous alkaline washing liquid to obtain a H₂S-depleted gas stream and a hydrogensulphide-comprising aqueous stream;
- (e) contacting the hydrogensulphide-comprising aqueous stream obtained in step (d) with sulphide-oxidizing bacteria in the presence of oxygen in a oxidation reactor

to obtain a containing slurry and a regenerated aqueous alkaline washing liquid;

(f) separating at least part of the containing slurry obtained in step (e) from the regenerated aqueous alkaline washing liquid and;

(g) recycling regenerated aqueous alkaline washing liquid obtained in step (e) to the H₂S-removal zone in step (d).

(Fig.)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.